Cobalt Cluster-Directed, Mn(III)-Mediated Chemo- and Stereoselective Radical Reactions of 1-Alken-3-ynes

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A new strategy has been developed to effect selective $Mn(OAc)_3$-mediated oxidative cycloaddition reactions of 1-alken-3-ynes with β-dicarbonyl compounds. The three-step sequence involves (1) protection of the triple bond of the substrate with the $-Co_2(CO)_6$ group, (2) Mn-promoted radical addition of the β-dicarbonyl compounds with the complexed enyne, and (3) oxidative demetalation. Mono-, di-, and tricycles, containing 2,3-dihydrofuran and tetrahydrofuran rings, are produced by exclusive attack on the uncomplexed C=C in moderate overall yields; formation of bi- and tricyclic derivatives occurs with excellent *cis*-stereoselectivity. Molecular mechanics calculations indicate that the *cis* ring fusion in these systems is thermodynamically favored. Reactions of the Co-complexed substrates proceed with Mn(III) promotion alone, whereas the free enynes require combined Mn(III)/Cu(II) mediation to produce furan derivatives, apparently reflecting the relative ease of oxidation of the respective intermediate radicals to carbocations. For the complexed substrates direct experimental proof for the formation of free carbocations along the reaction coordinate has been obtained by methanol trapping.

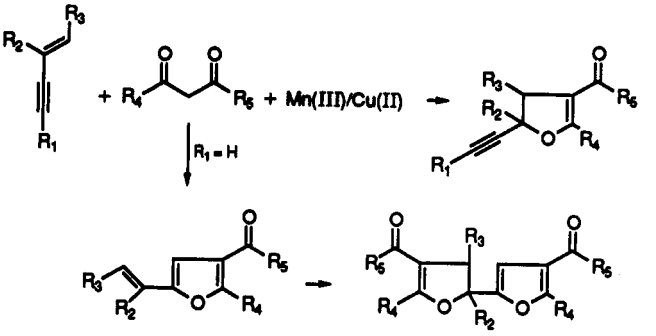
Introduction

Manganese(III)-mediated reactions of conjugated systems (e.g., 1,3-alkadienes, 1,3-alkadiynes, 1-alken-3-ynes) with β-dicarbonyl compounds have been extensively investigated during the past decade.[1] Enynes produce tri- and tetrasubstituted 2,3-dihydrofurans, furans, and/or 2,3-dihydrofuran-2-yl furans (Scheme 1) with chemoselectivity which is highly dependent on the type and degree of substitution of the substrate. When grouped according to their selectivity, they form three pairs, reacting nonchemoselectively (0-, 2-substituted) and chemoselectively at the triple (1,2-disubstituted, 1-substituted) or double bonds (4-substituted, 2,4-disubstituted).

The main objective of this study was to develop a general chemoselective approach *directing exclusive participation of the double bond*, thus drawing our attention to 0-, 1-, and 2-substituted and 1,2-disubstituted derivatives of 1-buten-3-yne. The initial step of our strategy was to protect the triple bond with the $-Co_2(CO)_6$ moiety, a function which has been demonstrated in electrophilic additions to the C=C of complexed enynes[2] and in nucleophilic coupling reactions of (propargylium)$Co_2(CO)_6^+$ complexes.[3] Selective functionalization of 1-alken-3-ynes at the double bond, leaving the triple bond untouched, would allow subsequent modification of these adducts taking advantage of the synthetic versatility of the triple bond.

A second objective was to establish the stereochemistry of the process, especially with respect to the influence of the $-Co_2(CO)_6$ unit. This also offered us the opportunity to investigate the nature of *cobalt-complexed propargyl radicals* since such species would be generated from the

Scheme 1



R_1, R_2, R_3 = H, Alk; R_4, R_5 = Alk, OEt

Mn-promoted addition of the β-dicarbonyl radical to the complexed enyne. The formation of (propargyl)$Co_2(CO)_6$ radicals as intermediates has been postulated in the reactions of propargyl halides with $Co_2(CO)_8$[4] and in the reactions of Co-complexed propargyl acetates with Grignard reagents.[5] Although we[3] and others[6] have demonstrated the remarkable stability and considerable synthetic utility of Co-complexed propargyl cations, no systematic studies of the stability, electronic character, or synthetic potential of the corresponding or other α-organometallic radicals[7,8] have been reported.

Our intention was also to look closer at the mechanism of the Mn(III)-mediated reactions, in particular to address some of the most debatable issues, e.g., the possible formation of intermediate carbocations preceding the

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(2) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475.
(3) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207.
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(7) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904.

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cyclization step.[1] The essence of the Mn(III)-mediated interaction of unsaturated substrates with carbonyl compounds consists of a one-electron oxidation of the latter and subsequent addition of α-oxo- and α,α-dioxoalkyl radicals to the substrate's multiple bond. The adduct radicals thus formed may convert to products either by H-atom abstraction or by interaction with the metal-oxidant resulting in oxidative ligand transfer, deprotonation or cyclization.

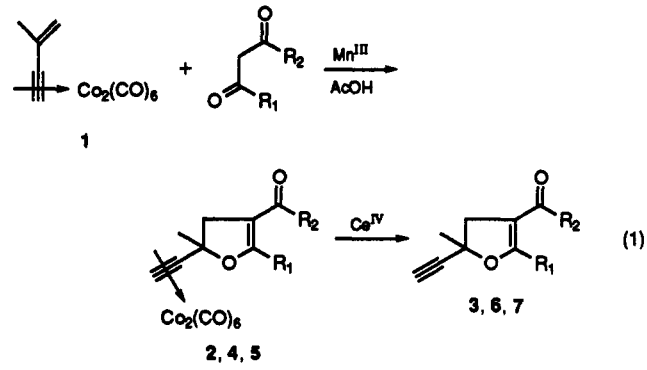
Finally, we were most interested in expanding the synthetic scope of the reaction, providing entry to complex polycyclic furanoid structures with the future aim to use this methodology in natural product synthesis.

Results and Discussion

Synthetic Studies: Acyclic 1-Alken-3-ynes. The initial step of the strategy adopted was to protect the triple bond with the $-Co_2(CO)_6$ moiety. To serve effectively the latter has to survive the subsequent Mn(III)-promoted reaction. Two potential problems were anticipated in this respect: (1) Mn(III)-induced oxidative demetalation of the $-Co_2(CO)_6$ group, precedented by known Fe(III),[2] Ce(IV),[9] and R_3NO[10] decomplexation, and (2) thermal destruction/decomplexation, since the Mn-promoted reactions are typically conducted between 23 and 115 °C.[1] Furthermore, if coordination of the Co-complexed substrate or intermediates with the oligomeric $Mn(OAc)_3$[11] is required,[1] steric retardation could result from the substantial steric demand of the $-Co_2(CO)_6$ unit. Thus, the requirement for effective radical reactions of the double bond of $Co_2(CO)_6$-protected 1-alken-3-ynes is that the rate of the Mn(III)-mediated cycloaddition must be substantially faster than that of the oxidative/thermal demetalation.

Optimization for acyclic enynes was carried out for the reaction between methyl acetoacetate and isopropenylacetylene complex 1 (eq 1).[12] The molar ratio of substrate/$Mn(OAc)_3$ (1:1, 1:2, 1:4, 1:8) as well as the reaction temperature (20, 30, 45 °C) were varied to achieve complete conversion with minimal demetalation. By these criteria, the optimal conditions found were substrate/$Mn(OAc)_3$ (1:4), at 30 °C, and a reaction time of 30 min. Since the concentration of Mn(III) is crucial for these reactions,[1] we maintained it at 0.3 M uniformly during this study. Under these conditions dihydrofuran **2** was obtained in 65% isolated yield together with 8% of decomplexed product **3**. Complete demetalation of **2** was accomplished with $(NH_4)_2Ce(NO_3)_6$, producing **3** in an overall yield of 59%.

The scope of the reaction with complexed acyclic enynes was then expanded to include representative acyclic and



(1)

2,3 (R_1 = Me, R_2 = OMe); **4,5** (R_1 = R_2 = Me); **5,7** (R_1 + R_2 = $(CH_2)_3$)

cyclic β-diketones. 2,4-Pentanedione and 1,3-cyclohexanedione were cycloadded to 1 affording 2,3-dihydrofuran **4** (52%) and hydrobenzofuranone **5** (46%), respectively, accompanied by modest amounts of decomplexed products (**6**, 6%, and **7**, 10%). It is noteworthy that no products were isolated which would indicate any decomplexation of 1 *prior* to radical addition (isopropenylacetylene itself reacts at both the double and triple bonds).[1]

Cyclic 1-Alken-3-ynes. The incorporation of cyclic enynes as substrates constituted the next step toward extending the scope of Mn-promoted radical cycloadditions to the synthesis of di- and tricyclic systems. This also provided an opportunity to investigate the stereoselectivity of the process, especially with respect to the influence of the $-Co_2(CO)_6$ unit. Using cyclohexenylacetylene complex **8** it was found that the reaction with methyl acetoacetate did not achieve full conversion under the protocol utilized for acyclic substrates. Such retardation, induced by a β-alkyl substituent, could be expected on the basis of previous findings.[13,14] By varying the substrate/$Mn(OAc)_3$ molar ratio and the temperature, the conditions were optimized (substrate/$Mn(OAc)_3$ 1:6, 30 °C, 2.5 h) to provide full conversion with minimal decomplexation and reasonable reaction time. Thus, from **8** and methyl acetoacetate hexahydrobenzofuran **9** was isolated in 22% yield as a single stereoisomer. Attempts to improve the yield by addition of $Cu(OAc)_2$ (equimolar through 3-fold excess) were not successful, indicating that the reason for the low yield is not the sluggish oxidation of the intermediate cyclic propargyl radical by $Mn(OAc)_3$. The product **9** is assigned a *cis* stereochemistry based on spectroscopic and X-ray correlation studies (*vide infra*). Reaction of **9** with $(NH_4)_2Ce(NO_3)_6$ smoothly released *cis*-**10** in 82% yield.

In contrast, the reaction of uncomplexed cyclohexenyl acetylene **11** with acetoacetic ester occurs chemoselectively *at the triple bond* to produce furan **12**.[14] An excess of reagent converts the primary product to tricycle **13**. No hydrobenzofuran **13** was isolated in the reaction of complex **8**, showing that the reactions of Co-complexed cyclic 1,3-enynes complement those of the uncomplexed substrates, allowing one to take full advantage of the synthetic versatility of the multiple bonds (Figure 1). The reversal of chemoselectivity observed indicates that decomplexed product **10**, isolated together with Co complex **9**, is derived from the latter and not formed from **8** by decomplexation–radical cycloaddition.

Under the protocol optimized for complex **8** cyclopentenyl acetylene complex **14** showed significantly higher

(8) α-Cp_2Fe: Baker, C.; Horspool, W. M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1862, 2294. $CpCo(\eta^5\text{-}C_7H_9)^+$: Geiger, W. E.; Genneth, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352. α-(Arene)$Cr(CO)_3$: Top, S.; Jaouen, G. *J. Organomet. Chem.* **1987**, *336*, 143. Kirss, R. U.; Treichel, P. M.; Haller, K. J. *Organometallics* **1987**, *6*, 242. (Pentadienyl)$Fe(CO)_3$: Sapienza, R. S.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Organomet. Chem.* **1976**, *121*, C35. Pearson, A. J.; Chen, Y.-S.; Daroux, M. L.; Tanaka, A. A.; Zettler, M. *J. Chem. Soc., Chem. Commun.* **1987**, 155. α-(Alkynyl)$Cp_2Mo_2(CO)_4$: Le Berre-Cosquer, N.; Kergoat, R.; L'Haridon, P. *Organometallics* **1992**, *11*, 721.

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(11) Hessel, L. W.; Romers, C. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 545.

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(13) Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980**, *36*, 701.

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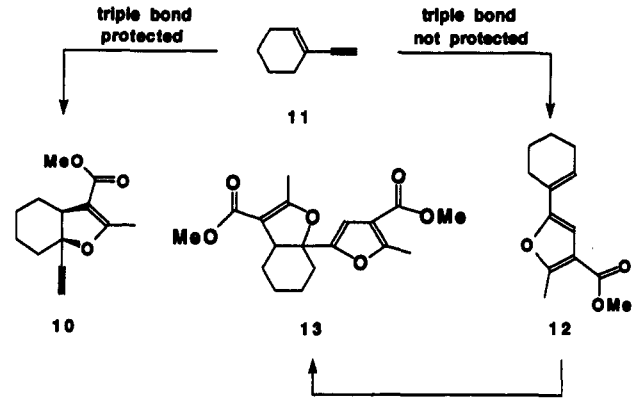
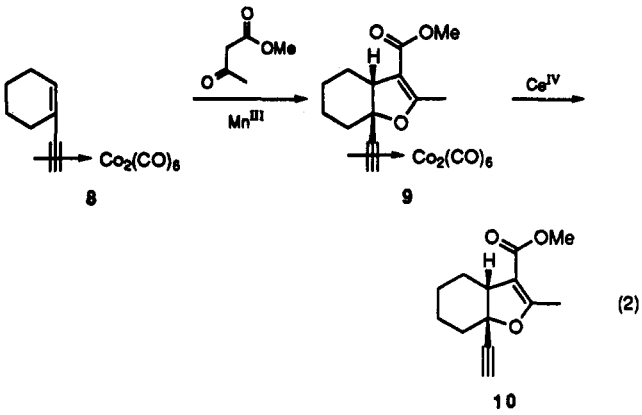
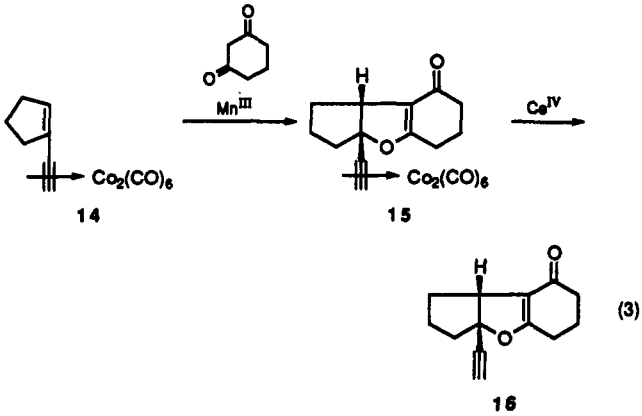


Figure 1.



reactivity (possibly derived from increased ring strain), full conversion to **15** (28%) and **16** (10%) being achieved within 1 h at 30 °C. It is noteworthy that the combined yield of **15** and **16** was almost twice as high as that obtained in the reaction of the cyclohexenyl complex **8**. Once again, the reaction is highly stereoselective, producing a single stereoisomeric tricycle **15** assigned the *cis*-configuration based on spectroscopic correlation with analogues characterized by X-ray diffraction (*vide infra*).



Our next objective was to investigate the influence of the $-Co_2(CO)_6$ unit on the stereochemistry of cyclization by conducting parallel reactions with the same substrates in both complexed and uncomplexed forms. Appropriate model compounds are 1,3-enynes which react chemoselectively at the double bond in their uncomplexed form. Cyclohexenyl and cyclopentenyl acetylene themselves are not suitable since they initially react chemoselectively at the triple bond.[1] A decade ago, however, one of us showed that the bulky dimethylhydroxymethyl group effectively

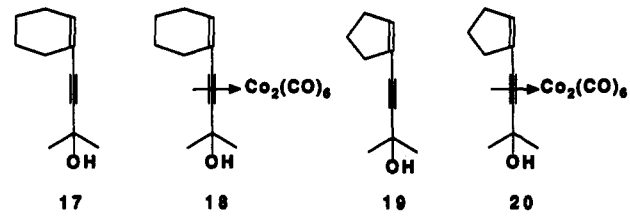
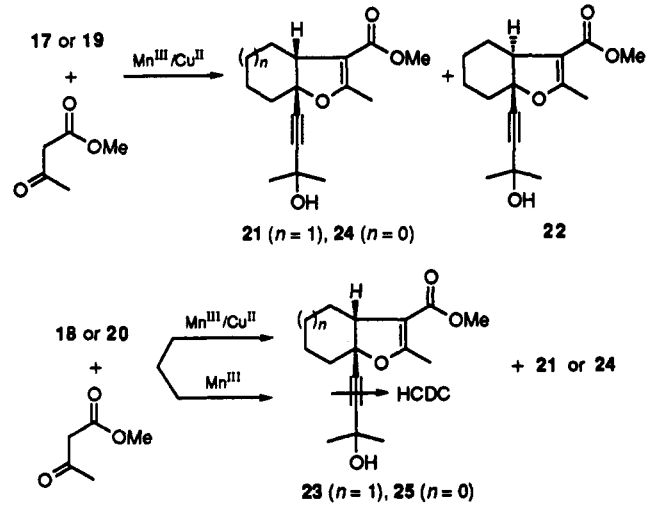


Figure 2.

Scheme 2



protects a triple bond against radical attack.[1] On the basis of this fact, we focused on a comparison of enynes **17** and **19** and their $-Co_2(CO)_6$ complexes **18** and **20**.

The reaction of substrate **17** with acetoacetic ester using the Mn^{III}/Cu^{II} oxidative system produced the expected cyclization product (25%) as a mixture of geometrical isomers **21**/**22** in the ratio of 89:11. In contrast, the corresponding Co complex **18** gave a *single* stereoisomer **23** along with a comparable amount of decomplexed **21** in a total yield of 40%. The stereochemistry of **23** was unambiguously established as *cis* by X-ray diffraction (*vide infra*). Additional study showed that the stereoselectivity does not depend on whether Mn(III) alone or both Mn(III) and Cu(II) acetates are used together. Control experiments demonstrated that **21** and **23**, as well as a mixture of **21** and **22**, are stable toward isomerization under the reaction conditions. Molecular mechanics calculations (MMX, PCMODEL) of the total energy of **21** and **22**, as well as their Co complexes, showed the greater stability of *cis*-isomers both in complexed (ΔE = 15 kcal) and uncomplexed (ΔE = 7 kcal) forms. All together these data allow one to conclude that the reaction is occurring under kinetic control and (but) producing the thermodynamically more stable isomers. Thus, the experiments with cyclohexenyl acetylenes **17** and **18** demonstrate that the metal cluster enhances the stereoselectivity of addition to the double bond causing also the appreciable increase in the yield (25% versus 40%).

On the other hand, both free and complexed cyclopentenyl acetylenes **19** and **20** upon Mn/Cu-promoted reaction with methyl acetoacetate afforded single isomers **24** and **25**, respectively. However, once again the influence of complexation on the yield was substantial: 47% of **24** from **19** vs a total of 78% of **24** and **25** from **20**. MMX calculations indicated the greater stability of complexed (ΔE = 33 kcal) and uncomplexed (ΔE = 17 kcal) *cis*-isomers

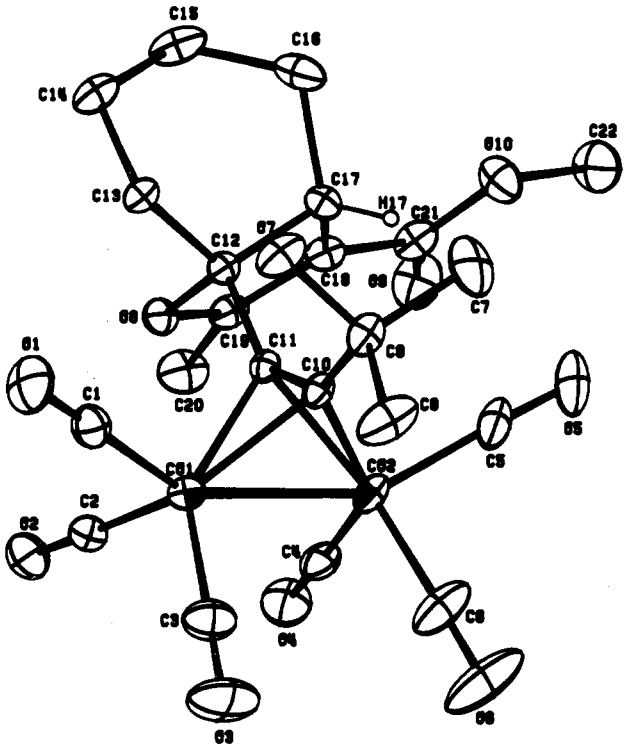


Figure 3. ORTEP diagram of compound 23.

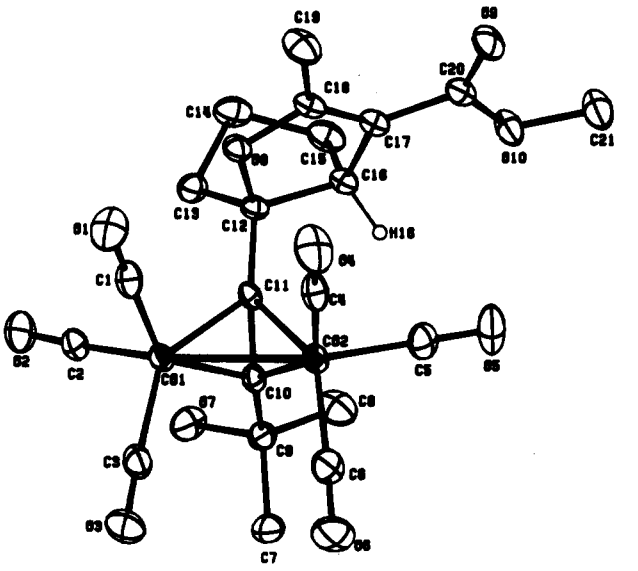


Figure 4. ORTEP diagram of compound 25.

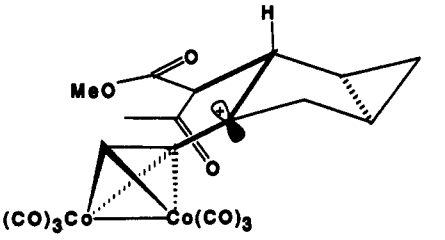


Figure 5.

with the energy difference being greater in the [3.3.0] than in the [4.3.0] systems (16 vs 8 kcal).

Stereochemical Assignments. To establish the configuration of the cyclization products **10**, **16**, **21**, and **24** (and hence their cobalt complexes), we intended to use the bridgehead ^3J(C,H) coupling constants as a structural tool.[15,16] A literature search, however, indicated that the reference coupling constants involving (C_{sp},H) coupling through an sp^3–sp^3 carbon pair had not been reported. The ^3J(≡CCCH) values for **10**, **16**, **21**, and **24** were determined by the *selective decoupling technique*,[15] and all fell in the range of 5.0–6.0 Hz, in the unreliable region where ^3J(C,H) coupling constants for geometrical isomers often overlap.[15,16] In the absence of opposite isomers the only independent proof of configuration was X-ray diffraction. Accordingly, single-crystal X-ray diffraction structure determinations of the conveniently crystalline complexes **23** and **25** were carried out. The resulting ORTEP diagrams, depicted in Figures 3 and 4, clearly show in each case the *cis*-orientation of the bridgehead H and the (alkynyl)$Co_2(CO)_6$ units. Other noteworthy structural features of **23** and **25** include (1) a dramatically bent geometry for the coordinated alkyne unit (α = 142° for **23** and 143° for **25**) and a lengthened coordinated C–C bond (1.33 Å for both complexes vs 1.21 Å for C≡C), consistent with significant rehybridization of and extensive Co back-bonding to the coordinated alkyne; (2) a boatlike conformation of the cyclohexane ring of **23**; (3) occupancy of a pseudoequatorial position by the –(alkynyl)$Co_2(CO)_6$ unit at the bridgehead in **23** and **25**; and (4) a somewhat twisted torsion angle of 22° between the bridgehead C–H (C17–H17) and bridgehead C–C (C12–C11) bonds in **23** and a corresponding angle of 16° in the bicyclo[3.3.0] system **25**.

Thus, the *cis*-stereochemistry determined for complexes **23** and **25** allows assignment of the same stereochemistry for decomplexed **21**, **24** and **10**, **16**, all of which have comparable ^3J(C,H) values. We also conclude that ^3J(C,H) values of 5.0–6.0 Hz correspond to *cis*-isomers for [3.3.0] and [4.3.0] bicyclic systems involving (C_{sp},H) coupling through an sp^3–sp^3 carbon unit.

A putative transition state leading to *cis*-fused [3.3.0] and [4.3.0] products is depicted in Figure 5. It is favored by the pseudoequatorial disposition of the bulky (alkyne)-$Co_2(CO)_6$ group and the β-dicarbonyl moiety with the latter approaching the carbocationic center from the pseudoaxial direction. We note also here a recent report by Grove and co-workers[17] in which a high selectivity for *cis*-fused products was found in cyclizations forming bicyclic [4.3.0] systems via intramolecular Friedel–Crafts alkylations of (propargylium)$Co_2(CO)_6^+$ complexes. For comparison, it should be mentioned that in the case of pure radical cyclizations *cis*-fused carbocycles are also preferentially formed, if the bond to one of the ring junction atoms is made last.[18]

Mechanistic Considerations. A suggested mechanism for the Mn-promoted addition of a β-dicarbonyl compound to enyne complex **1** is provided in Scheme 3. Taken collectively, previous studies indicate that Mn-promoted β-dicarbonyl additions occur by a complex, multistep

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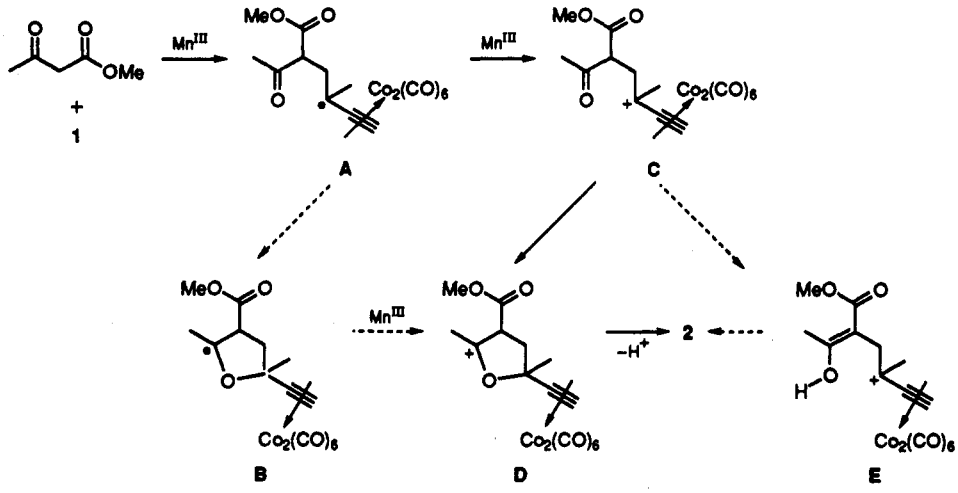
Scheme 3

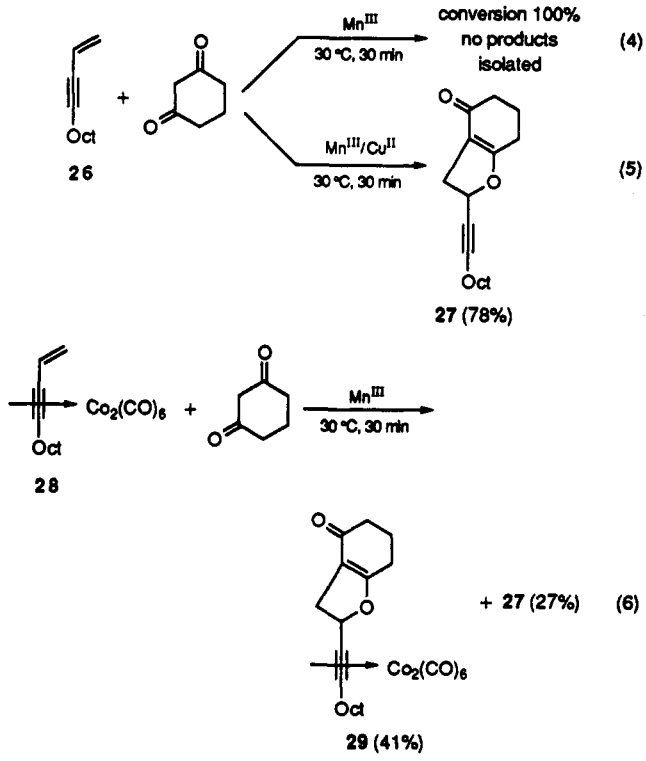


process involving essentially generation of a β-dicarbonyl radicaloid species, its addition to the olefin substrate, possible oxidation of the adduct radical, cyclization of the radical or carbocation, and proton/H-atom abstraction.[1] The rate dependence on the unsaturated component[19] suggests that C–C bond formation is the rate-determining step.[20] At several stages of the process Mn and/or Cu may be associated with reactive intermediates.

To obtain a deeper understanding of the process, we designed and carried out a set of experiments designed to establish (1) whether Co-complexed propargyl radical **A** cyclizes directly to **B** or is first oxidized to generate carbocation **C**, (2) whether free carbocations **C** and **D** are formed along the reaction coordinate or the formation of dihydrofuran **2** takes place within the $Mn^{III}(Cu^{II})$–ligand sphere, and (3) whether carbocation **C** is the direct precursor of the cyclized species **D** or whether enolization to **E** occurs prior to cyclization.

Addressing the first issue, we conducted two sets of experiments. In the first the reactions of 1-dodecen-3-yne (**26**) with 1,3-cyclohexanedione, mediated by $Mn(OAc)_3$ alone and in the presence of co-oxidant, $Cu(OAc)_2$ were compared (eqs 4 and 5 in Scheme 4). With $Mn(OAc)_3$ alone complete consumption of starting compound occurred within 30 min at 30° but no products could be isolated, apparently the result of gross polymerization (gelatinous material observed). On the other hand, using a combination of $Mn(OAc)_3/Cu(OAc)_2$ produces hydrobenzofuranone **27** in 78% yield. The reason for this striking difference is attributed to the relative ability of the Mn(III) and Cu(II) ions to oxidize alkyl radicals to the corresponding carbocations with the latter approximately 250 times more reactive.[21] The initiation step and the formation of the C–C bond can occur with the participation of Mn(III) alone, determining the rate of consumption of starting compound. The presence of $Cu(OAc)_2$ becomes crucial after the formation of propargyl adduct–radical. Since Mn(III) ion is not powerful enough to oxidize the resulting radicals to the corresponding carbocations, the former are not able to attack the carbonyl group, which would produce cyclization product. Thus, the only pathway for radical consumption is unfruitful polymerization.

Scheme 4



In the presence of Cu(II) the propargyl adduct–radical is oxidized to propargyl carbocation, which sequentially converts to cyclization product **27**.

The second set of experiments is represented by eqs 4 and 6 in Scheme 4. In contrast to substrate **26**, its cobalt complex **28** undergoes cyclization (to **29** and **27**) not only in the presence of $Cu(OAc)_2$ but also *when $Mn(OAc)_3$ is used alone*. The use of catalytic or equimolar amounts of $Cu(OAc)_2$ did not affect the yield. We believe these features reflect the lower oxidation potential of Co-complexed propargyl radicals compared with their uncomplexed counterparts, derived from the remarkable stability of the incipient (propargylium)$Co_2(CO)_6$ cations.[3] Supporting this conclusion is the fact that those few substrates which add β-dicarbonyls with Mn promotion alone are ones which possess carbocation-stabilizing groups at the incipient radical center.[22]

These two sets of experiments indicate that the *propargyl adduct radicals are oxidized to carbocations* (**A**

(19) Vinogradov, M. G.; Pogosyan, M. S.; Steinshneider, A. Ya.; Nikishin, G. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1981**, *30*, 1703.
(20) Snider, B. B.; Patricia, J. J.; Kates, S. A. *J. Org. Chem.* **1988**, *53*, 2137.
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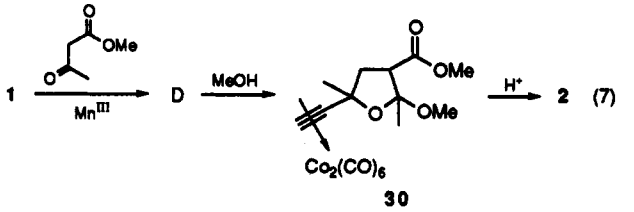
→ C, Scheme 3) *either by $Mn(OAc)_3$ or $Cu(OAc)_2$ prior to the cyclization step.*

To address the second issue we chose the reaction shown in Scheme 3 as a model and ran it in MeOH, expecting that if free carbocations formed they could be trapped by solvent if the cyclization step was sufficiently slow. On the other hand, if cyclization occurs in the Mn sphere, trapping would not be expected. Use of alcohols as solvents in Mn(III)-mediated reactions has been very limited.[1] In particular, ethanol was recently used to modify intramolecular Mn-promoted additions to alkenes and was found to be an effective *H-atom donor* (in the absence of $Cu(OAc)_2$), converting primary as well as secondary adduct-radicals to saturated products.[23,24] Thus, H-atom delivery from solvent to propargyl radical **A** could also occur prior to oxidation to carbocation **C**. We also pursued a purely synthetic interest: the development of an experimental protocol with methanol as solvent could expand the scope of the Mn(III)-mediated reactions of 1-alken-3-ynes by allowing the use of acid-sensitive substrates.

The reaction of isopropenylacetylene complex **1** was carried out using Mn promotion alone and with combined Mn/Cu promotion. In either case the reaction rate was unchanged in methanol (30 °C, 30 min) and led to the formation of methoxy-substituted tetrahydrofuran **30** as a mixture of three stereoisomers. The yields are the same in the case of both protocols, indicating again that Mn(III) is able to oxidize the Co-complexed propargyl radicals as effectively as $Cu(OAc)_2$. No other products, derived from H-atom transfer to propargyl radical, methanol trapping of propargyl carbocation **C**, or deprotonation of cyclic carbocation **D** (producing **2**), were detected by careful ^{13}C NMR analysis of the crude product. That trapping product **30** is formed directly from intermediate **D** and not via methanol addition to dihydrofuran **2** was supported by demonstrating the nonreactivity of **2** toward MeOH/HOAc. The fact that carbocation **C** was not trapped with MeOH is consistent with either cyclization in the coordination sphere of Mn or with faster cyclization of the free carbocation compared with trapping rate. Nonetheless, isolation of ether **30** *provides unambiguous evidence of free carbocation intermediates and formation of dihydrofurans outside the metal ion ligand sphere.* We also converted product **30** to **2** (86%) by treatment with a 3-fold excess of CF_3COOH (rt, 30 min).



The successful trapping of carbocation **D** allowed us to address the third issue, i.e., whether the β-dicarbonyl moiety participates in the cyclization step in its keto or its enol form (**C** and **E** in Scheme 3). In the latter case, tetrahydrofuran **30** would not be formed and the reaction would produce 2,3-dihydrofuran **2** directly. The absence of **2**, its nonreactivity toward MeOH/HOAc (above), and the isolation of **30** indicates that *intermediate cation C undergoes attack directly by the carbonyl group* and cyclization is not preceded by enolization.

Conclusions

A generally applicable chemoselective method has been developed for Mn(III)-mediated oxidative cycloaddition of β-dicarbonyl compounds to the C–C double bond of 1-alken-3-ynes utilizing the $-Co_2(CO)_6$ unit as a chemo-, regio-, and stereo-directing group. Moderate yields of mono-, bi-, and tricyclic 5-alkynyldihydrofuran derivatives are obtained. Reactions with cyclic en–yne and/or β-dicarbonyl components are highly *cis*-stereoselective, the selectivity being enhanced by $-Co_2(CO)_6$ complexation in the [4.3.0] system. The reactions of the Co-complexed substrates proceed with Mn(III) promotion alone, whereas the free en–ynes require combined Mn(III)/Cu(II) mediation to produce significant yields of furan derivatives. This contrast appears to reflect the relative ease of oxidation of the respective intermediate radicals to carbocations. For the complexed substrates direct experimental proof for the formation of free carbocations along the reaction coordinate has been obtained by methanol trapping. Studies underway are aimed at utilizing these reactions in the synthesis of furanoid natural products and at the exploration of other radical reactions modulated by organometallic fragments.

Experimental Section

General. All reactions were performed under an atmosphere of dry N_2. Analytical instruments, spectral calibrations and chromatographic materials were previously described.[25] Analytical TLC was performed on silica gel IB-F plates (Baker-flex); visualization was accomplished with UV illumination (254 nm) or by immersion in aqueous $KMnO_4$ solution followed by thorough washing. GC–MS were obtained on a HP 5985 GC/MS system with SE-54 Econo-Cap capillary columns (30 m × 0.32 mm, 1.0-μm film). *J* values are given in Hz. Abbreviations: PE, pentane; E, ether.

The starting alkynes and their cobalt complexes were synthesized according to the following procedures: 2-methyl-1-buten-3-yne and cyclohexenyl- and cyclopentenylacetylenes, by dehydration of commercially available (Lancaster) alcohols;[26] 1-dodecen-3-yne (**26**), by alkylation of 1-buten-3-yne with octyl iodide;[26] propargyl alcohols **17** and **19**, by condensation of the corresponding 1-alken-3-ynes with acetone;[26] and (enyne)$Co_2(CO)_6$ complexes, by reaction of the corresponding 1-alken-3-ynes with $Co_2(CO)_8$ in benzene or ether.[27] $MgSO_4$ was used as a drying agent.

General Protocol A: Mn-Promoted Addition to Co-Complexed Acyclic 1-En-3-ynes. [4-Carbomethoxy-2,5-dimethyl-2-ethynyl-2,3-dihydrofuran]dicobalt Hexacarbonyl (2). The reaction flask was charged with $Mn(OAc)_3 \cdot 2H_2O$ (2.47 g, 9.2 mmol) under an inert atmosphere. After five pump-and-fill cycles, a solution of complex **1** (0.81 g, 2.3 mmol) and methyl acetoacetate (2.13 g, 18.4 mmol) in glacial AcOH (31 mL) was added in one portion [molar ratio substrate:Mn(III):β-dicarbonyl compound = 1:4:8]. The mixture was heated for 30 min at 30 °C (TLC monitoring) and then diluted with H_2O (30 mL) and extracted with ether (3 × 50 mL). The combined ethereal extracts were neutralized with saturated Na_2CO_3, washed (H_2O, 3 × 30 mL), and dried. The ether was evaporated, and the residue was chromatographed on SiO_2 (70 g, PE/E (15:1)) to give **2** (700 mg, 65%) as dark red crystals together with decomplexation product

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3 (33 mg, 8%). If $Cu(OAc)_2$ was used (5 mol %), yields were 62% of 2 and 14% of 3; with an equimolar amount of the former the yields were 65% and 10%, respectively. Mp: 90–91 °C. R_f = 0.52 (PE/E (5:1)). ^1H NMR ($CDCl_3$): δ 1.68 (s, 3H), 2.18 (t, 3H, J = 1.6), 2.85 (dq, 1H, J = 14.5, 1.6), 3.05 (dq, 1H, J = 14.5, 1.6), 3.67 (s, 3H), 6.05 (s, 1H). MS-DIP: 438 (18), 298 (100). Anal. Found: C, 41.35; H, 2.52. $C_{16}H_{12}O_9Co_2$ requires: C, 41.20; H, 2.58.

General Protocol B: Demetalation of (Alkyne)$Co_2(CO)_6$ Complexes. 4-Carbomethoxy-2,5-dimethyl-2-ethynyl-2,3-dihydrofuran (3). A solution of $Ce(NH_4)_2(NO_3)_6$ (3.3 g, 6.0 mmol) in dry acetone (18 mL) was slowly added to a solution of complex 2 (700 mg, 1.50 mmol) in dry acetone (10 mL) at −78 °C. After addition was complete, the solution was allowed to warm over 30 min to rt and stirred for 1 h. The reaction mixture was poured into saturated NaCl solution, extracted with ether (3 × 30 mL), and dried. The ether was evaporated, and the residue was chromatographed on SiO_2 (7 g, PE/E (10:1)) to give 3 (211 mg, 78%). Bp (K): 69–71 °C/6 mm. R_f = 0.48 (PE/E (5:1)). ^1H NMR ($CDCl_3$): δ 1.64 (s, 3H), 2.20 (t, 3H, J = 1.5), 2.63 (s, 1H), 2.88 (dq, 1H, J = 14.3, 1.5), 3.21 (dq, 1H, J = 14.3, J = 1.5), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$): 14.1, 28.4, 44.0, 50.9, 73.0, 79.1, 84.9, 100.8, 166.0, 166.3. IR (neat): 3300, 2120, 1702, 1648. MS: M^+ 180. Anal. Found: C, 66.87; H, 6.60. $C_{10}H_{12}O_3$ requires: C, 66.67; H, 6.67.

[4-Acetyl-2,5-dimethyl-2-ethynyl-2,3-dihydrofuran]dicobalt Hexacarbonyl (4). Using protocol A 1.27 g (3.6 mmol) of 1 gave compound 4 (835 mg, 52%) as dark-red crystals together with decomplexation product 6 (35 mg, 6%). Mp: 63–64 °C. R_f = 0.45 (PE/E (1:1)). ^1H NMR ($CDCl_3$): δ 1.70 (s, 3H), 2.16 (s, 3H), 2.21 (s, 3H), 2.91 (d, 1H, J = 15.0), 3.15 (d, 1H, J = 15.0), 6.06 (s, 1H). MS-DIP: M^+ 422 (2), 282 (79). Anal. Found: C, 42.44; H, 2.65. $C_{16}H_{12}O_8Co_2$ requires: C, 42.67; H, 2.67.

4-Acetyl-2,5-dimethyl-2-ethynyl-2,3-dihydrofuran (6). Protocol B carried out on 1.77 mmol of 4 afforded 6 (208 mg, 72%). R_f = 0.40 (PE/E (1:1)). ^1H NMR ($CDCl_3$): δ 1.66 (s, 3H), 2.20 (s, 3H), 2.23 (t, 3H, J = 1.5), 2.63 (s, 1H), 2.95 (dq, 1H, J = 14.3, 1.5), 3.28 (dq, 1H, J = 14.3, 1.5). ^{13}C NMR ($CDCl_3$): 14.9, 28.4, 29.3, 44.7, 73.1, 79.0, 84.7, 111.2, 165.4, 193.9. IR (neat): 3280, 3230, 2100, 1668, 1618, 1598. MS-DIP: M^+ 164. Anal. Found: C, 73.29; H, 7.15. $C_{10}H_{12}O_2$ requires: C, 73.17; H, 7.32.

2-Ethynyl-2-methyl-2,3,4,5,6,7-hexahydrobenzofuran-4-one]dicobalt Hexacarbonyl (5). Using protocol A 2.7 mmol of 1 and cyclohexandione gave 5 (575 mg, 46%) as dark-red crystals together with decomplexation product 7 (45 mg, 10%). Mp: 103–104 °C dec. R_f = 0.30 (PE/E (1:3)). ^1H NMR ($CDCl_3$) 1.74 (s, 3H), 2.03 (m, 2H), 2.34 (t, 2H, J = 7.0), 2.41 (t br, 2H, J = 6.1), 2.80 (d, 1H, J = 14.7), 3.03 (d, 1H, J = 14.5), 6.07 (s, 1H). MS-DIP: M^+ 434 (7), 294 (48). Anal. Found: C, 44.02; H, 2.55. $C_{17}H_{12}O_8Co_2$ requires: C, 44.16; H, 2.60.

2-Ethynyl-2-methyl-2,3,4,5,6,7-hexahydrobenzofuran-4-one (7). With protocol B 1.16 mmol of 5 afforded 7 (158 mg, 78%). Bp (K): 85–86 °C/0.9 mm. R_f = 0.25 (PE/E (1:3)). ^1H NMR ($CDCl_3$–ac-d_6): δ 1.69 (s, 3H), 2.07 (quintet, 2H, J = 6.2), 2.34 (m, 2H), 2.46 (m, 2H), 2.83 (d spl, 1H, J = 14.3), 2.88 (s, 1H), 3.11 (d spl, 1H, J = 14.3). ^{13}C NMR ($CDCl_3$, ac-d_6): 21.0, 23.3, 27.9, 35.7, 40.2, 73.8, 82.0, 83.8, 111.4, 174.6, 194.4. IR (neat): 3280, 3230, 2120, 1648, 1625 br. MS-DIP: M^+ 176. Anal. Found: C, 74.59; H, 6.91. $C_{11}H_{12}O_2$ requires: C, 75.00; H, 6.82.

General Protocol C. Mn-Promoted Addition to Co-Complexed Cyclic 1-Alken-3-ynes. [*cis*-3-Carbomethoxy-7a-ethynyl-2-methyl-3a,4,5,6,7,7a-hexahydrobenzofuran]-dicobalt Hexacarbonyl (9). The reaction flask was charged with $Mn(OAc)_3·2H_2O$ (4.02 g, 15 mmol) under nitrogen. After five pump-and-fill cycles a solution of complex 8 (0.98 g, 2.5 mmol) and methyl acetoacetate (3.48 g, 30 mmol) in a glacial AcOH (50 mL) was added in one portion [molar ratio substrate:Mn(III): β-dicarbonyl compound = 1:6:12]. The mixture was heated for 2.5 h at 30 °C with stirring (TLC monitoring). Workup and isolation were carried as in protocol A (PE/E (20:1)) to give 9 (0.275 g, 22%) as dark-red crystals together with 10 (16 mg, 3%). Mp: 80–82 °C. R_f = 0.54 (PE/E (5:1)). ^1H NMR ($CDCl_3$): δ 1.34–1.67 (m, 5H), 1.70–1.92 (m, 2H), 1.99–2.10 (m, 1H), 2.22 (s, 3H), 2.90 (t br, 1H, J = 5.2), 3.65 (s, 3H), 6.03 (s, 1H). MS-DIP: 478 (10), 338 (43). Anal. Found: C, 44.90; H, 3.22. $C_{19}H_{16}O_9Co_2$ requires: C, 45.06; H, 3.16.

***cis*-3-Carbomethoxy-7a-ethynyl-2-methyl-3a,4,5,6,7,7a-hexahydrobenzofuran (10).** Protocol B carried out using 0.54 mmol of 9 gave 10 (97 mg, 82%). R_f = 0.42 (PE/E (5:1)). ^1H NMR ($CDCl_3$): δ 1.30–1.40 (m, 1H), 1.42–1.62 (m, 4H), 1.88–1.97 (m, 2H), 2.04–2.12 (m, 1H), 2.22 (d, 3H, J = 1.2), 2.50 (s, 1H), 3.20 (t br, 1H, J = 6.1), 3.72 (s, 3H). ^{13}C NMR ($CDCl_3$): 14.5, 19.1, 19.4, 25.9, 32.5, 47.6, 50.7, 71.7, 81.9, 85.7, 107.7, 166.2, 167.2. Selective decoupling: J(HC≡CC$_{7a}$C$_{3a}$H) = 6.0. IR (neat): 3300, 2120, 1700, 1640 cm^{-1}. MS-DIP: M^+ 220. Anal. Found: C, 70.82; H, 7.20. $C_{13}H_{16}O_3$ requires: C, 70.91; H, 7.27.

[*cis*-1,8-Didehydro-3-ethynyl-2-oxatricyclo[6.4.0.0^{3,7}]-dodecan-9-one]dicobalt Hexacarbonyl (15). According to protocol C, from 14 (1.02 g, 2.7 mmol), $Mn(OAc)_3·2H_2O$ (4.34 g, 16.2 mmol), and 1,3-cyclohexanedione (3.63 g, 32.4 mmol) in AcOH (54 mL) with a reaction time of 1 h, workup and subsequent column chromatography (SiO_2, 200g, PE/E (1:2)) gave 15 (370 mg, 28%) as dark-red crystals together with 16 (56 mg, 10%). Mp: 130–135 °C dec without melting. R_f = 0.48 (PE/E (1:3)). ^1H NMR ($CDCl_3$): δ 1.56–1.73 (m, 1H), 1.75–2.10 (m, 7H), 2.26–2.38 (m, 2H), 2.40–2.54 (m, 2H), 3.25 (d, 1H, J = 7.3), 6.05 (s, 1H). MS-DIP: 488 (1), 320 (26). Anal. Found: C, 46.60; H, 2.72. $C_{19}H_{14}O_8Co_2$ requires C, 46.72; H, 2.87.

***cis*-1,8-Didehydro-3-ethynyl-2-oxatricyclo[6.4.0.0^{3,7}]-dodecan-9-one (16).** Protocol B using 0.64 mmol of 15 afforded 16 (111 mg, 86%). R_f = 0.39 (PE/E (1:3)). ^1H NMR (ac-d_6): δ 1.45–1.57 (m, 1H), 1.71–1.90 (m, 3H), 1.93–2.09 (m, 4H), 2.21–2.29 (m, 2H), 2.39–2.50 (m, 2H), 3.38 (s, 1H), 3.55 (d, 1H, J = 7.9). ^{13}C NMR (ac-d_6): 22.5, 24.2, 24.7, 32.9, 37.3, 43.1, 53.8, 77.1, 84.3, 92.6, 115.7, 176.2, 194.4. Selective decoupling: J(HC≡CC$_7$C$_{11}$H) = 5.0. IR (neat): 3290, 3230, 2115, 1648, 1632, 1620. MS-DIP: M^+ 202. Anal. Found: C, 77.02; H, 6.89. $C_{13}H_{14}O_2$ requires: C, 77.23; H, 6.93.

***cis*- and *trans*-3-Carbomethoxy-7a-(3′-hydroxy-3′-methyl-1′-butynyl)-2-methyl-3a,4,5,6,7,7a-hexahydrobenzofurans (21, 22).** According to protocol C from 17 (0.328 g, 2.00 mmol), methyl acetoacetic ester (2.78 g, 24 mmol), $Mn(OAc)_3·2H_2O$ (3.22 g, 12 mmol), and $Cu(OAc)_2$ (399 mg, 2.00 mmol) in glacial AcOH (40 mL) after column chromatography (60 g, PE/E (3:1, 2:1)) isomers 21 and 22 (141 mg, 25%) were obtained. GC–MS (100 °C (3 min) → 5°/min → 280 °C (15 min)): 11% 22 (t_R = 25.8 min, M^+ 278 (2)), 89% 21 (t_R = 26.4 min, M^+ 278 (15)). In the NMR spectrum the only distinguishable peaks are as follows: 21 3.16 (t, 1H, H-3a, J = 6.2), 22 3.22 (t, 1H, H-3a, J = 6.3). Full spectral data for 21 are given below.

[*cis*-3-Carbomethoxy-7a-(3′-hydroxy-3′-methyl-1′-butynyl)-2-methyl-3a,4,5,6,7,7a-hexahydrobenzofuran]dicobalt Hexacarbonyl (23). (1) According to protocol C, from 18 (900 mg, 2 mmol), methyl acetoacetate (2.78 g, 24 mmol), and $Mn(OAc)_3·2H_2O$ (3.22 g, 12 mmol) in glacial AcOH (40 mL) after column chromatography (90 g, PE/E (5:1, 3:1)) was obtained 23 (300 mg, 27%) as dark-red crystals together with 21 (110 mg, 20%, ~100% purity by GC–MS). Mp: 100–102 °C. R_f = 0.63 (PE/E (1:1)). ^1H NMR ($CDCl_3$): 1.40–2.02 (m, 8H), 1.60 (s, 3H), 1.61 (s, 3H), 2.06 (s, 1H), 2.21 (s, 3H), 3.23 (t unresolved, 1H, J = 4.8), 3.67 (s, 3H). MS-DIP: 536 (4), 396 (100). Anal. Found: C, 46.90; H, 3.94. $C_{22}H_{22}O_{10}Co_2$ requires: C, 46.81; H, 3.90. Single crystals for X-ray analyses (Figure 3) were obtained by methanol vapor diffusion into a pentane solution of 23.

(2) The experiment described in (1) was modified with $Cu(OAc)_2$ (399 mg, 2 mmol) to give 23 (250 mg, 22%) and 21 (100 mg, 18%, purity ~100% by GC–MS).

***cis*-3-Carbomethoxy-7a-(3′-hydroxy-3′-methyl-1′-butynyl)-2-methyl-3a,4,5,6,7,7a-hexahydrobenzofuran (21).** Protocol B was carried out with 0.4 mmol of 23 affording 21 (91 mg, 80%, purity ~100% by GC–MS). R_f = 0.43 (PE/E (1:1)). ^1H NMR ($CDCl_3$): 1.30–1.60 (m, 4H), 1.48 (s, 6H), 1.78–2.05 (m, 4H), 2.18 (s, 3H), 3.16 (t, 1H, J = 6.2), 3.69 (s, 3H). ^{13}C NMR ($CDCl_3$): 14.2, 18.6, 18.8, 25.0, 32.2, 30.8, 47.4, 50.3, 64.5, 81.8, 83.1, 88.3, 106.6, 165.9, 166.9. HR-FAB calcd for $C_{16}H_{22}O_4$ (M^+ − 1) 277.1440 found 277.1443. Selective decoupling: J(C≡CC$_{7a}$C$_{3a}$H) = 5.7. MS-DIP: M^+ 278.

***cis*-3-Carbomethoxy-6a-(3′-hydroxy-3′-methyl-1′-butynyl)-2-methyl-1-oxabicyclo[3.3.0]octane (24).** According to protocol C, 19 (300 mg, 2 mmol), $Mn(OAc)_3·2H_2O$ (3.22 g, 12 mmol), methyl acetoacetate (2.78 g, 24 mmol), and $Cu(OAc)_2$ (399 mg, 2 mmol) in glacial AcOH (40 mL) after a reaction time of 1 h,

workup, and column chromatography (18 g, PE/E (3:1)) afforded **24** (247 mg, 47%). GC–MS (50 °C (5 min) → 10°/min → 280 °C (10 min)): t_R = 28.47 min, isomeric purity ~100% for both crude and isolated samples. R_f = 0.52 (PE/E (1:1)). ^{1}H NMR ($CDCl_3$): 1.49 (s, 6H), 1.62–2.25 (m, 6H), 2.17 (d, 3H, J = 1.5), 3.59 (d, 1H, J = 7.4), 3.68 (s, 3H). ^{13}C NMR ($CDCl_3$): 14.2, 24.0, 33.6, 42.8, 31.3, 50.8, 55.3, 65.2, 82.3, 89.2, 90.8, 105.0, 166.2, 167.5. MS-DIP: M^+ 264. HR-FAB: calcd for $C_{15}H_{20}O_4$ (M^+) 264.1362, found 264.1364.

[*cis*-3-Carbomethoxy-6a-(3′-hydroxy-3′-methyl-1′-butynyl)-2-methyl-1-oxabicyclo[3.3.0]octane]dicobalt Hexacarbonyl (25). According to protocol C, from **20** (872 mg, 2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (3.22 g, 12 mmol), methyl acetoacetate (2.78 g, 24 mmol), and $Cu(OAc)_2$ (399 mg, 2 mmol) in glacial AcOH (40 mL) after a reaction time of 1 h, workup, and subsequent column chromatography (60 g, PE/E (5:1)) was obtained **25** (668 mg, 61%) as dark-red crystals together with **24** (88 mg, 17%, isomeric purity ~100% by GC–MS). Mp: 87–89 °C. R_f = 0.65 (PE/E (1:1)). ^{1}H NMR ($CDCl_3$): 1.60 (s, 3H), 1.61 (s, 3H), 1.60–2.35 (m, 6H), 1.93 (s, 1H), 2.20 (d, 3H, J = 1.3), 3.43 (d, 1H, J = 7.0), 3.68 (s, 3H). MS-DIP: 522 (7), 382 (100). Anal. Found: C, 46.06; H, 3.65. $C_{21}H_{20}O_{10}Co_2$ requires: C, 45.82; H, 3.64. Single crystals for X-ray analyses (Figure 4) were obtained by methanol vapor diffusion into a pentane solution of **25**.

[2-(1′-Decyn-1′-yl)-2,3,4,5,6,7-hexahydrobenzofuran-4-one]dicobalt Hexacarbonyl (29). Using protocol A 2.6 mmol of **28** gave **29** (600 mg, 41%) as a red oily liquid together with decomplexation product **27** (190 mg, 27%). R_f = 0.64 (PE/E 1:3). MS-DIP: M^+ 561 (M+1, 14%), 392 (13%). Anal. Found: C, 51.26; H, 4.58. $C_{24}H_{26}O_8Co_2$ requires C, 51.43; H, 4.64.

2-(1′-Decyn-1′-yl)-2,3,4,5,6,7-hexahydrobenzofuran-4-one (27). (1) Using protocol B on 1.07 mmol of **29** afforded **27** (262 mg, 89%). Bp (K): 155–158 °C/0.55 mm. R_f = 0.41 (PE/E (1:3)). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, J = 6.6), 1.27 (s br, $4CH_2$), 1.36 (m, 2H), 1.52 (quintet, 2H, J = 7.2), 2.04 (m, 2H), 2.24 (td, 2H, J = 7.2, 1.5), 2.35 (t, 2H, J = 6.6), 2.45 (m, 2H), 2.85 (dd, 1H, J = 14.3, 7.9), 3.11 (dd, 1H, J = 14.3, 10.7), 5.33 (ddt, 1H, J = 10.7, 7.9, 1.5). ^{13}C NMR ($CDCl_3$): 13.9, 18.6, 21.5, 22.5, 28.1, 28.7, 28.9, 29.0, 31.7, 23.8, 34.2, 36.3, 74.0, 77.5, 88.8, 112.6, 176.2, 195.0. IR (neat): 2220, 1655, 1638 br. MS-DIP: M^+ 274. Anal. Found: C, 79.00; H, 9.35. $C_{18}H_{26}O_2$ requires: C, 78.83; H, 9.49.

(2) According to protocol A from **26** (426 mg, 2.6 mmol), 1,3-cyclohexanedione (2.33 g, 20.8 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.79 g, 10.4 mmol), and $Cu(OAc)_2$ (519 mg, 2.6 mmol) in glacial acetic acid (35 mL) after chromatography on SiO_2 (60 g, PE/E (1:1)) was obtained **27** (558 mg, 78%).

[3-Carbomethoxy-2,5-dimethyl-5-ethynyl-2-methoxytetrahydrofuran]dicobalt Hexacarbonyl (30). (1) A mixture of **1** (704 mg, 2 mmol), methyl acetoacetate (1.86 g, 16 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (2.14 g, 8 mmol) in dry MeOH (35 mL) was heated for 30 min at 30 °C (TLC control) under nitrogen. Solvent was evaporated on a Schlenk-line, ether was added to the residue, and the suspension was filtered. The filtrate was evaporated, and the residue was chromatographed (SiO_2, 70 g, PE/E (10:1)) to give **30** as dark-red crystals (460 mg, 46%). Anal. Found: C, 41.01; H, 3.21. $C_{17}H_{16}O_{10}Co_2$ requires: C, 40.96; H, 3.21. The ^{13}C NMR of **30** consisted of three stereoisomers in the ratio 1:1:2. PTLC (PE/E (5:1), three runs) gave the more mobile spot as the major fraction, consisting of two isomers in the ratio of 1:2. The less mobile, minor component was a single stereoisomer.

Major Fraction. Mp: 91–93 °C. R_f = 0.55 (PE/E (5:1)). ^{1}H NMR ($CDCl_3$): main isomer 1.54, 1.67 (s, s, 3H, 3H), 2.15 (dd, 1H, J = 12.9, 8.2), 2.88 (t, 1H, J = 12.4), 3.10 (dd, 1H, J = 11.8, 8.4), 3.24 (s, 3H), 3.71 (s, 3H), 6.00 (s, 1H); minor isomer 1.31, 1.63 (s, s, 3H, 3H), 2.18–2.61 (m, 3H), 3.29 (s, 3H), 3.72 (s, 3H), 6.03 (s, 1H). ^{13}C NMR (C_6D_6): main isomer 21.3, 32.8, 42.7, 48.6, 51.8, 55.7, 72.4, 84.5, 104.2, 108.0, 169.5, 200.0; minor isomer 20.5, 31.0, 43.7, 49.3, 51.7, 56.1, 72.7, 84.4, ~104.0, 109.9, 172.2, 200.0. MS-FAB: 498 (M^+ 1), 483, 470, 442, 414, 386, 358, 330 (48%), 299 (parallel fragmentation pattern 467, 382, 354, 326, 299).

Minor Fraction. Mp: 68–70 °C. R_f = 0.50 (PE/E (5:1)). ^{1}H NMR ($CDCl_3$): 1.55, 1.58 (s, s, 3H, 3H), 2.25 (dd, 1H, J = 12.2, 7.3), 2.69 (t, 1H, J = 12.5), 3.14 (dd, 1H, J = 12.6, 7.3), 3.22 (s, 3H), 3.70 (s, 3H), 6.06 (s, 1H). ^{13}C NMR (C_6D_6): 22.3, 30.4, 43.3, 49.5, 51.7, 55.3, 73.7, 83.7, 104.3, 108.0, 169.3, 200.9. MS-FAB: M^+ 498 (0), the rest is the same as for the major fraction.

(2) The procedure described in item 1 when modified by inclusion of $Cu(OAc)_2$ (0.40 g, 2.0 mmol) gave **30** (44%) consisting of the same stereoisomers as above.

Conversion of 30 to 2 by reaction with trifluoroacetic acid. A solution of CF_3COOH (48 mg, 0.42 mmol) in dry benzene (1.5 mL) was slowly added via syringe to a solution of **30** (70 mg, 0.14 mmol) in dry benzene (5 mL) at +5 °C under N_2. The solution was allowed to warm to rt, and the mixture was stirred for 30 min (TLC monitoring). The solvent was evaporated on a Schlenk-line, and the residue was dissolved in PE/E (5:1) and filtered through a short bed of silica gel to give **2** (56 mg, 86%).

X-ray Structure Determination of 23 and 25. X-ray structure determinations were performed on an Enfaf-Nonius CAD-4 diffractometer using monochromated Mo Kα radiation (λ = 0.710 69 Å). The atomic scatterings factors were taken from the International Tables for X-ray Crystallography, and the structures were solved by the heavy atom method and refined by the full-matrix least-squares method (SHELX-76).

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Supplementary Material Available: Preparation and spectroscopic data for starting propargyl alcohols and corresponding Co-complexes (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Atomic coordinates, bond lengths and angles, thermal parameters and structure factors for compounds **23** and **25** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.